— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

Method of electroplating a workpiece having high-aspect ratio holes

5   Specification:

The production of high-aspect ratio printed circuit boards, for example so-called back panels, poses well-known problems for good quality electrolytic copper metallization. The panels can be from 3 mm and up to 10 mm thick with aspect

10   ratios of typically 10 : 1. However, there is a current trend requiring even thicker panels and with an aspect ratio up to 15 : 1. Such panels typically can be larger than "normal" production panels which gives added problems in handling due to their weight. One of the limiting factors in copper deposition is the mass transport of ions into the high-aspect ratio holes. Achieving the required copper

15   thickness in the hole without over-plating the surface causing resist over-plating with pattern plate or poor line definition with panel plate are the main problems in the production of high-aspect ratio panels. A further factor with back panels is the difficulty of component mounting using the press-fit technique when the copper deposit distribution is poor. To overcome throwing power problems low

20   electroplating current densities have been used which obviously have a negative impact on productivity. As a solution to these problems reverse pulse plating can allow the use of higher current densities with improved surface distribution and throwing power in the through-holes as described in DE 42 25 961 C2 and DE 27 39 427 A1.

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In horizontal processing of printed circuit boards it has emerged that the high-aspect ratio throwing power in Uniplate® (Atotech Deutschland GmbH) systems has been a restriction to their use for the production of thicker panels. Even for panels thicker than 1.6 mm the copper throwing power has not been fully

30   acceptable depending on the aspect ratio. The reasons for this have been because of the emphasis on the production of thinner material at higher current densities with blind micro-vias. The high-current density, in the order of 10 A/dm² average and the requirement to produce blind micro-vias under such conditions has required the use of relatively high-copper concentrations at

above 35 g/l. Both of these factors have not enabled the best throwing power in high-aspect ratio panels. Trials have been made to improve the throwing power in standard Inpulse® (Atotech Deutschland GmbH) equipment. But these have only given a marginal improvement. These trials were limited by the pulse

5   parameters which are available with the standard Inpulse® system (copper plating system with inert anodes, using the iron(II)/iron(III) redox system and reverse pulse current technique in vertical and horizontal plating devices).

Kruse describes in Galvanotechnik (3/2002, p.680) a method for reverse pulse

10   plating of e.g. printed circuit boards, in which the sum of the duration of two forward pulses intermitted by an off pulse has been set to 5 – 250 ms, and the duration of reverse pulses has been set to 0 – 5 ms.

In US 2003/0019755 A1 a method for pulsed electroplating a metal on a

15   substrate is described wherein an electrodeposition (cathodic) pulse may range from about 500 - 3000 ms, while that for an electrodissolution (anodic) pulse may range from about 1 – 300 ms.

In reverse pulse plating printed circuit boards, the duration of forward pulses

20   often has been set to 10 – 80 ms, and duration of reverse pulses has been set to 0.5 – 6 ms. This has resulted in a frequency range of about 12 to about 95 Hz. If printed circuit boards have been to be produced which were 2 mm thick and which contained through holes with an aspect ratio of 10 : 1 acceptable throwing power of copper deposition in the through holes has been

25   achieved at a current density in the range of 1 – 10 A/dm² for the forward pulses and at a current density in the range of 10 – 40 A/dm² for the reverse pulses. If printed circuit boards with a thickness of greater than 2 mm have been to be produced, the current densities must be decreased in order to achieve an acceptable result in throwing power.

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In a joint project with the Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V., Germany, the flow dynamics of copper deposition was investigated. The results from this investigation have been published by Reents, B., Thies, A., Langheinrich, P.: "Online measurement of flow and mass transfer in micro-holes

with PIV and an electrochemical sensor array". Proc. ISE Symp., 2002, Düsseldorf, Germany. The influences on copper deposition in blind micro-vias have been documented as part of these experiments and have been published by Reents, B., Kenny, S.: "The influence of fluid dynamics on plating electrolyte

5   for the successful production of blind micro-vias". IPC Expo 2002 Proc. of the Techn. Conf. IPC, Northbrook, III., USA (2002).

From the above it is apparent that a main problem in electroplating printed circuit boards with high-aspect ratio through holes is to achieve a sufficient

10   metal plating thickness in the hole. At the same time it is mandatory to run electroplating at a minimum average current density at the printed circuit board in order to ensure adequate efficiency of the process which may only be garantueed if the through-put and hence plating current density is high-enough. Finally also good surface quality must be ensured which means that the metal

15   deposit produced must be as even and shiny as possible.

The object of the present invention is therefore to fulfill the above requirements and more specifically to achieve sufficient metal plating thickness in high-aspect ratio printed circuit boards. Another object of the present invention is also to

20   ensure that electroplating efficiency is as high as possible which implies that metal plating current density at the printed circuit boards must be as high as possible. A suitable average plating current density is held to be at least 1.7 A/dm², more preferably at least 2 A/dm² and most preferably at least 3 A/dm².

25   The solution to this object is achieved by the method of electroplating a workpiece comprising high-aspect ratio holes according to claim 1. Preferred embodiments of the invention are outlined in the subordinate claims.

The method according to the present invention serves to electroplate a

30   workpiece which is preferably plate-shaped such as a printed circuit board and which has high-aspect ratio holes. The method comprises the following method steps:

   a. The workpiece is brought into contact with a metal plating electrolyte and at least one anode.

   b. A voltage is applied between the workpiece and the anodes, to the effect that a current flow is provided to the workpiece. The current flow generated is a pulse reverse current flow. The pulse reverse current has a frequency of at most about 6 Hertz, preferably at most 4 Hertz and more preferably at most 2.5 Hertz. In each cycle time of the pulse reverse current flow at least one forward current pulse and at least one reverse current pulse are provided.

Preferably in one cycle time of the pulse reverse current flow one forward current pulse and one reverse current pulse are provided.

In a preferred embodiment the ratio of the duration of the forward current pulses to the duration of the reverse current pulses of one cycle is set to at least 5, more preferably to at least 15 and still more preferably to at least 18. This ratio may be set to at most 75 and more preferably to at most 50. The ratio may most preferably be set to about 20.

The duration of the forward current pulses of one cycle may preferably be set to at least 100 ms, more preferably to at least 160 ms and most preferably to at least 240 ms.

The duration of the reverse current pulses of one cycle may preferably be set to at least 0.5 ms, more preferably to at least 8 ms and most preferably to at least 12 ms.

The peak current density at the workpiece of the forward current pulses may be set to at least 3 A/dm². It may be set to at most 15 A/dm². Most preferably the peak current density at the workpiece of the forward current pulses may be about 5.5 A/dm².

The peak current density at the workpiece of the reverse current pulses may especially be set to at least 10 A/dm². It may be set to at most 60 A/dm². Most

preferably the peak current density at the workpiece of the reverse current pulses may be in the range of from about 16 to about 20 A/dm².

5 In a preferred embodiment the ratio of the peak current density of the forward current pulses to the peak current density of the reverse current pulses may be set to at least 1, more preferably to at least 2 and still more preferably to at least 3. This ratio may be set to at most 15 and more preferably to at most 4. The ratio may most preferably be set to about 3.

10 In a preferred embodiment of the present invention the rise times of the forward and reverse current pulses, respectively, may be adjusted depending on the technical objective pursued.

The workpiece is preferably plate-shaped. It may more preferably be a printed 15 circuit board or any other plate-shaped electrical circuit carrier, such as a semiconductor wafer (integrated circuit) or any hybrid (IC-) chip carrier like a multi-chip module.

In a preferred embodiment of the present invention the method comprises the 20 following method steps:

a. A first voltage is applied to between a first side of the workpiece and at least one first anode, to the effect that a first pulse reverse current flow is provided to the first side of the workpiece, said first pulse reverse current 25 flow having at least one first forward current pulse and at least one first reverse current pulse flowing in each cycle time.

b. A second voltage is applied to between a second side of the workpiece and at least one second anode, to the effect that a second pulse reverse current flow is provided to the second side of the workpiece, said second 30 pulse reverse current flow having at least one second forward current pulse and at least one second reverse current pulse flowing in each cycle time.

As to this last embodiment the first forward and reverse current pulses of one cycle may be offset relative to the second forward and reverse current pulses of one cycle, respectively. In a more preferred embodiment of the present invention this offset between the first current pulses and the second current

5 pulses is approximately 180°.

For further improving throwing power the current flow may comprise, in each cycle time, two forward current pulses with one zero current break between the two forward current pulses and one reverse current pulse.

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In another embodiment for improving throwing power the current flow may comprise, in each cycle time, one forward current pulse followed by one reverse current pulse and after that one zero current break.   ·

15 In another embodiment for improving throwing power the current flow may comprise, in each cycle time, one forward current pulse followed by one reverse current pulse without any zero current break in this cycle.

In still another embodiment for improving throwing power the current flow may

20 comprise, in each cycle time, one forward current pulse, followed by one zero current break and after that one reverse current pulse.

Of course there are still more combinations possible according to the order or the occurrence of the different pulses and the zero current breaks. Furthermore

25 it is possible to combine different cycles.

Depending on the durations of the different current pulses and where required of zero current breaks an average current density I_{av} can be specified in relation to the cycle time. The average current density can be calculated by the

30 following equation:

$$I_{av} = \frac{\sum_i I^i_{fw} * t^i_{fw} - \sum_j I^j_{rv} * t^j_{rv}}{t_{ct}} ,$$

wherein further:

I_{fw} = forward current density,

5   I_{rv} = reverse current density,

t_{fw} = forward pulse duration,

t_{rv} = reverse pulse duration, wherein i,j = integers ≥ 1, which denote individual
forward and reverse pulses, respectively, in each pulse cycle, and

t_{ct} = cycle time, wherein a cycle time can additionally comprise the time of zero
10   current break pulses if such zero current break pulses are used.

Preferably the average current density may be set in a range of 1 to 10 A/dm², more preferably 2 to 6 A/dm² and most preferably 3 to 5 A/dm². Preferably the average current density is set to a value of about 4 A/dm².

15

Further in the course of metal plating the workpiece, at least one parameter of the pulse reverse current flow, selected from the group comprising the ratio of the duration of the forward current pulses to the duration of the reverse current pulses of one cycle and the ratio of the peak current density of the forward

20   current pulses to the peak current density of the reverse current pulses of one cycle, may be varied. More specifically it turns out to be advantageous to increase, in the course of metal plating the workpiece, the ratio of the peak current density of the forward current pulses to the peak current density of the reverse current pulses and/or to decrease the ratio of the duration of the

25   forward current pulses to the duration of the reverse current pulses.

Another improvement of the invention comprises bringing the workpiece into contact with the metal plating electrolyte by delivering the metal plating electrolyte towards the surface of the workpiece at an electrolyte flow velocity

30   relative to the surface of the workpiece. The metal plating electrolyte is preferably forced under agitation towards the workpiece. More preferably the electrolyte flow velocity at the surface of the workpiece comprises a velocity component normal to the surface of the workpiece being at least 1 m/sec.

Preferably the velocity may be set to at least about 1.4 m/sec, more preferably to at least about 7.2 m/sec. It may be set to be at most about 11.5 m/sec.

In a further improvement of the present invention the method comprises
5   providing at least one anode being inert and dimensionally stable.

Anodes are preferably used which contain titanium or tantalum as the basic material, which is preferably coated with noble metals or oxides of the noble metals. Platinum, iridium or ruthenium, as well as the oxides or mixed oxides of
10   these metals, are used, for example, as the coating. Besides platinum, iridium and ruthenium, rhodium, palladium, osmium, silver and gold, or respectively the oxides and mixed oxides thereof, may also basically be used for the coating. A particularly high resistance to the electrolysis conditions could be observed, for example, on a titanium anode having an iridium oxide surface, which was
15   irradiated with fine particles, spherical bodies for example, and thereby compressed in a pore-free manner. Moreover, of course, anodes may also be used, which are formed from noble metals, for example platinum, gold or rhodium or alloys of these metals. Other inert, electrically conductive materials, such as carbon (graphite), may also basically be used. These anodes are
20   provided in order to reduce the excessive polarisation voltage and to keep the anodes electrically conductive and also, at the same time, to protect the anodes from electrolytic sputtering.

In practical usage the insoluble anode can be made from an expanded metal
25   sheet of titanium, which was activated with noble metal (e.g. platinum).

In another usage a rod-like anode can extend into tubular cathodes. To enlarge the effective surface of the anodes, the cathodes may be formed from a tubular expanded metal which, at the same time, renders possible a very good
30   exchange of electrolyte as a consequence of the lattice structure.

When using inert and dimensionally stable anodes for performing conventional DC or pulse plating methods it has turned out that the anodes got corroded after some time of usage and that the organic additives added to the bath were

increasingly consumed. This has now been attributed to the evolution of gas generated both at the workpiece and at the anodes. By using a low frequency pulse plating method, e.g. at 6 Hertz or even lower, and especially by setting either the forward or the reverse current pulse or both to a time duration as long

5   as possible such detrimental effects can be avoided.

According to one specific embodiment of the present invention the metal plating electrolyte may be a copper plating electrolyte.

10   In this latter case, and especially if the at least one anode is inert and dimensionally stable, copper ions may be replenished to the electrolyte by dissolving copper metal. For this purpose the copper plating electrolyte may contain at least one compound capable of oxidizing copper metal to copper ions. Such oxidizing compound may be for example a ferric compound, such as

15   ferric ion, ferric sulphate more specifically. After addition of e.g. the iron-(II) sulphate heptahydrate to the electrolyte after a short time the effective iron-(II)/ iron-(III) redox system is formed, wherein iron-(II) sulphate heptahydrate is excellently suited for aqueous acid copper baths. The use of iron compounds with anions which lead in the copper electrolyte to undesired secondary

20   reactions such as for example chloride or nitrate may also not be used.

To regenerate the copper ions an ion generator is used, which contains parts of copper. The generator is separated from the electroplating chamber containing the anode. The electrolyte, which is weakened by a consumption of copper

25   ions, containing the compounds as e.g. iron-(II) sulphate, is guided past the anodes, whereby iron-(III) compounds are formed from the iron-(II) compounds. The electrolyte is subsequently conducted through the copper ion generator and thereby brought into contact with the copper parts. The iron-(III) compounds thereby react with the copper parts to form copper ions, i.e. the copper parts

30   dissolve. The iron-(III) compounds are simultaneously converted into the iron-(II) compounds. Because of the formation of the copper ions, the total concentration of the copper ions contained in the electrolyte is kept constant. The electrolyte passes from the copper ion generator back again into the

electroplating chamber in which it comes in contact with the workpiece and the anodes.

Preferably iron-(II) and iron-(III) compounds are used as the electrochemically
5   reversible redox system. Equally suitable are the redox systems of the following
elements: titanium, cerium, vanadium, manganese and chromium. They can be
added to the copper deposition solution for example in the form of titanyl
sulphuric acid, cerium(IV) sulphate, sodium metavanadate, manganese(III)
sulphate or sodium chromate. Combined systems can be advantageous for
10   special applications.

The concentrations of the compounds of the redox system must be set in such
a way that, through the resolution of the metal parts, a constant concentration of
the metal ions in the deposition solution can be maintained. This guarantees
15   that the insoluble anodes, coated with noble metals or oxides of the noble
metals, are not damaged.

As an alternative the oxidizing compound may also be oxygen. Oxygen,
contained in the air, is constantly introduced into the electrolytic fluid by
20   electrolyte movements so that oxygen dissolves in the fluid. This oxygen is also
capable of dissolving copper by oxidizing the copper parts in the ion generator,
wherein oxygen ions are formed.

Now, referring to the investigations outlined above, further experiments have
25   been carried out to investigate the influences on through-hole plating,
particularly in high-aspect ratio holes. Table 1 gives a summary of electrolyte
exchange mechanism considered and also the influencing factors.

The influencing parameters were held constant as far as possible, and the :-
30   artificial convection by means of forced flooding was investigated.

A specially designed multilayer printed circuit board with electrochemical flow
sensor was used as part of these investigations. A schematic of one test hole

on the test board is shown in fig. 1. This test board comprises a micro electrode array.

The test board was placed in a test chamber which allowed the variation of key
5   parameters as follows:

- Diameter of nozzle
- Angle a between beam of fluid and workpiece surface
- Distance between nozzle mouth and workpiece surface
10 - Lateral flow along the surface of the workpiece
- Pressure / Flow
- Density of the electrolyte
- Pulse pumping

15 The test chamber is shown in fig. 2. This test chamber is being used for hydrodynamic studies. The test chamber comprises a housing 1, which emcompasses an adjustable disc 2. On this disc 2 the test printed circuit board 3 is arranged in a vertical arrangement. The item with numeral 4 is a stopper. The electrochemical cell also comprises a counter electrode 5 and a reference
20 electrode 6, which both are also schematically displayed in fig. 1. A nozzle 7 serves to impinge metal plating electrolyte to the surface of the printed circuit board 5 at an angle a which is defined as the angle between the axis of the nozzle 7 and the upper right hand part of the test printed circuit board 3 as shown in this fig. Finally there is a lateral nozzle adjustment means 8 which
25 allows fine tuning of the point of impingement of the metal plating electrolyte at the test printed circuit board.

Fig. 3 shows a microsection through one test coupon having a hole with a diameter of 0.2 mm showing the inner layer electrode connections, the results
30 from experiments with this test coupon being given in fig. 4. This fig. illustrates the results of investigation of fluid velocity and spray angle a as a function of current I at the individual inner layer electrodes. The experiments have been carried out under the following conditions:

Ring electrodes being formed in the inner layer of the test coupon circular to the hole with d = 200 μm;

The aspect ratios of the holes contained in the test coupons being:

in fig. 4.A: 1.3 (upstream);

5   in fig. 4.B: 2.8 (middle);

in fig. 4.C: 4.4 (downstream);

The aspect ratio was calculated in each individual case as the ratio of the distance from the hole entry to the respective inner layer, which was located upstream of the middle of the hole, in the middle of the hole and downstream

10   the middle of the hole, respectively, to the hole diameter L_x = - 0.2 mm.

Fluid flow velocity $v_j(y)$ was as follows:

        1) 0.66 m/sec

15   2) 1.46 m/sec

        3) 3.7 m/sec

        4) 7,2 m/sec

        5) 11.5 m/sec

20   The curves in the diagrams in fig. 4 are designated with numerals 1, 2, 3, 4 and 5 to correspond to the above fluid flow velocities $v_j(y)$. The results show that a maximum diffusion current is achieved at a flow angle of 90° and of course with the highest impingement velocity.

25   In larger scale tests the technique of particle image velocimetry (PIV) was used to image the flow of electrolyte through a high-aspect ratio panel. Fig. 5 shows the experimental set-up (particle image velocimetry apparatus) used to carry out the tests. In this a dynamic system is illuminated by two laser beams, and the resulting interference pattern information is recorded on a camera.

30

The data obtained from one of the flow experiments through a high-aspect ratio panel are shown in fig. 6, which is an illustration of vertical solution flow through a high-aspect ratio panel. The individual arrows show the direction and size of velocity vectors at the respective locations in the examined area.

Therefore it can be concluded in general that the fluid flow velocity of electrolyte solution shall be selected such that it has a velocity component normal to the surface of the workpiece of at least 1 m/sec, preferably of at least 5 m/sec and most preferred of at least 10 m/sec.

The results from the experiments have enabled modifications made to the Uniplate® Inpulse® system to improve the production of blind micro-vias as reported.

Horizontal Application:

The standard Inpulse® module for horizontal processing of printed circuit boards (in which boards are conveyed in a horizontal path and in a horizontal plane of transport for processing same) but may also be conveyed in a vertical or any other plane of transport has a spray bar to cathode (workpiece) separation of 95 mm and an anode to cathode separation of 75 mm. In the Inpulse® 2 system both the spray bar and the anode are set much closer to the cathode at 15 mm and 8 mm for the anode. This enables a more intense electrolyte flow towards the panel and also has an added advantage making the use of anode shielding unnecessary whilst retaining excellent surface distribution. Also the spray system itself has been modified to give a more directed agitation towards the panel. These changes were made primarily to enable the more efficient flooding of blind micro-vias. Using this system experiments were made to investigate the optimal electrolyte composition and pulse plating parameters to achieve best throwing power in 3.2 mm thick panels with aspect ratio 10 : 1. The results have shown that primarily the pulse wave form set-up and the electrolyte adjustment may be individually important in giving throwing power improvement. The best electrolyte composition was found to be as follows:

Copper: 20 g/l
Sulphuric acid: 270 g/l
Chloride ions: 40 mg/l
Iron(II): 7 g/l

Iron(III): 1 g/l

Leveller Inpulse® H6: 1.7 – 2.0 ml/l

Brightener Inpulse®: 4.0 – 5.5 ml/l

5   Of course the metal plating electrolyte may vary to some extent. Throwing power may be efficiently improved if the electrical conductivity of the metal plating electrolyte is increased. This may be affected by increasing the acid concentration for example. The additive concentrations are more typical of electrolytes adjusted to produce high-aspect ratio panels. In particular the

10   copper concentration is 15 – 20 g/l lower than in a standard Inpulse® electrolyte.

The pulse plating parameters were varied from DC plating conditions at 4 A/dm² to pulse plating with forwards 250 ms and reverse 25 ms. A selection of the parameters used together with the throwing power achieved is shown in

15   Table 2.

Due to the weakness of corner flattening by means of high-reverse conditions and surface roughness, the best throwing power results were achieved with forwards 240 ms at a average current density of 4 A/dm² and reverse of 12 ms

20   at a reverse current density of 16 A/dm² and not with 25 ms in reverse time. A general tendency can be seen that with lower frequency the throwing power is increased, as is clearly illustrated in Table 3.

In all tests a phase shift in pulse parameter of 180° was used. This means that

25   the reverse pulse was applied to the anodes on one side of the test panel at the same time that the forward pulse was applied to the anodes on the other side. The pulse wave form schematic in fig. 7 (current as a function of time) illustrates this setting showing phase shift between top and bottom anodes (top curve: current at the top side of the cathode, bottom curve: current at the bottom side

30   of the cathode).

Microsection photographs of the panel produced in test 6 outlined in Table 2 are shown in fig. 8. In this case a 10 : 1 aspect ratio panel with thickness of 3.0 mm and hole diameter of 0.3 mm was electroplated. As can be seen at the centre of

the hole the thickness achieved is very low, the panel plate with the Inpulse® 2 system has a throwing power of approx. 70%.

As a comparison with similar panels, a throwing power of only 30 % would be
5 achieved at 3 A/dm² with horizontal DC. At 2 A/dm² a throwing power of 55 % is achieved under vertical conditions in DC. Only with pulse plating under standard vertical conditions with air agitation a throwing power of 90 % is achieved, but this is at an average current density of 2 A/dm². Using forced agitation improved throwing power is possible as discussed hereinbelow. But even this is not at
10 such a high-current density.

Vertical Application:

In vertical plating of workpieces metal plating electrolytes may be employed
15 which have the same composition as the metal plating electrolytes described above for horizontal processing. Likewise in vertical plating pulse plating may be performed under the same conditions as in horizontal processing. Therefore as to these plating conditions in vertical plating reference is made to the above description.
20

In vertical systems electrolyte agitation is usually made with a combination of air agitation in the electrolyte itself and a mechanical agitation of the circuit board being plated. This mechanical agitation must ensure that the panels are moved evenly and remain vertical in the electrolyte. Otherwise solution flow will not be
25 uniform through all the holes in the panel. To ensure this cathode movement, systems are used which clamp the panel securely and which are also used to supply current to the panel. These agitation systems, air in the electrolyte and movement of the panel, can lead to uneven fluid transport due to non-defined air agitation and due to the movement of the panel through the agitation
30 bubbles.

To overcome these problems the use of Eductors (spray nozzles which use the Venturi Principle, i.e. drawing of additional liquid through the nozzle is affected by the spray created, so that high-volume flow is achieved) is becoming more

common. Eductors using the Venturi Principle allow small pumps to circulate larger volumes of liquid. The kinetic energy of one solution will cause the flow of another. Typically the use of Eductors can give a 4 – 6 times increase in volume of solution movement when compared to the volume pumped. This increased

5   volume is however at a lower pressure than the directly pumped solution. Fig. 9 shows two sizes of commonly used Eductors in electrolytic copper plating systems. The smaller Eductor shown will pump a lower volume, but will allow more Eductors to be placed on one pipe, so giving a more even electrolyte flow.

10   Currently the method of installation of the Eductors in a vertical plating tank is on the floor underneath the cathode as shown in fig. 10, which shows the installation of Eductors in a vertical Inpulse® line in a view from the top of the installation to the bottom. At the bottom the Eductors 9 are disposed on a feeding pipe 10.

15

This installation is with two pipes placed one on each side below the cathode with the Eductors adjustable pointing upwards towards or away from the cathode. There are similar installations with the Eductors mounted on a single pipe running directly below the cathode and substantially parallel to the

20   cathode, the Eductors mounted at a fixed angle pointing alternately away from the panel. The disadvantages associated with this set-up are that the electrolyte flow uniformity depends on the positioning of the Eductors and also of the distance between the nozzle and the panel.

25   To give more uniform flow the Eductors can be positioned between the anodes in the plating cell pointing directly towards the cathode. This set-up has the advantage of giving a more direct flow of electrolyte towards the panel and is shown in fig. 11 as a view from the top of the installation to the side thereof. The Eductors 9 are shown to be disposed at the sides of the tank in front of the

30   anodes 11. The disadvantage of all Eductor installations is that the solution flow can never be completely uniform over the panel surface. A compromise must be made between the number of Eductors installed and flow uniformity.

To overcome the limitations of flow uniformity by the use of Eductors a moving spray system has been developed and is being tested in a trial tank in laboratory conditions. The system consists of a spray head which moves regularly over the surface of the cathode and produces an intensive forced

5 flooding of the panel and the through holes at the point of spraying. The head moves in a plane between anode and cathode and delivers the electrolyte in the direction towards the panel. It is so dimensioned that it does not interfere with the electrodeposition process. Results with high-aspect ratio panels have shown a significant improvement in throwing power when compared to standard

10 air agitation and a more uniform deposit in comparison to Eductor agitated equipment on the same scale. Fig. 12 shows plating results from a 3.0 mm panel with a 0.3 mm hole (aspect ratio: 10 : 1) using the moveable spray system. Average current density for electroplating was 2 A/dm². Throwing power was found to be 90 – 95 %. Reinforcement plating was performed by DC

15 plating in horizontal plating equipment at a current density of 5 A/dm².

Investigations have been continued in the use of so-called batch plating parameters to improve throwing power, particularly in panels thicker than 5 mm. During the plating cycle the pulse parameters are varied. Normally at the start of

20 the cycle a strong reverse charge is used to give a good throwing power followed by a lower reverse charge at the end of the plating cycle to give good surface finish. An example of such a plating sequence is given in Table 4.

Fig. 13 shows plating results from a 5.0 mm panel with a 0.5 mm hole (aspect

25 ratio 10 : 1) using a modified pulse plating sequence together with the moveable spray system to give optimal electrolyte exchange. The average current density applied is 1.7 A/dm². The throwing power was found to be 95 – 100 %.

Use of both optimized pulse parameters as well as electrolyte agitation gives

30 significant improvements in throwing power in trial line experiments.

Hence experiments in basic electrochemistry show a strong influence of electrolyte agitation on copper electroplating characteristics. Modifications to

horizontal Inpulse® equipment together with optimized plating parameters show improved throwing power under experimental conditions.

5   In vertical equipment use of Eductors to improve agitation is becoming a standard for new equipment. The use of a moving spray flood system shows advantages in the trial line scale for vertical systems.

Use of varying pulse parameters over the copper deposition time offers the possibility to improve throwing power with aggressive parameters whilst

10   retaining optimal surface finish using milder pulse parameters at the end of the processing time (cycle time).

It is to be understood that various modifications and substitutions by technical means may be applied to what has been described by way of the above

15   examples and of the drawings, without departing from the scope of the invention as defined by the appended claims. Further it is to be understood that various combinations of features described in this application will be suggested by the person skilled in the art and are to be included within the purview of this invention and within the scope of the appended claims. All publications, patents

20   and patent applications cited herein are hereby incorporated by reference.

Table 1: Electrolyte exchange mechanisms and influencing factors

5

Electrolyte exchange by	Influencing factors
• Diffusion • Migration • Natural Convection • Artificial Convection	• Concentration • Temperature • Surface Tension • Viscosity • Density

10

Table 2: Test conditions for Inpulse[®] 2 trials for 3.2 mm thick panels

Test	I average / I reverse [A/dm²]	Pulse Parameters in ms Forward / Reverse	Phase Shift [%]	Pulse Rise Time Factor	Surface Finish	Throwing Power min. [%]
1	4 DC	DC	-	-	Good	32
2	4 / 4	240 / 20	180	1.2	Good	53
3	4 / 16	80 / 4	180	1.2	Good	49
4	4 / 16	80 / 6	180	1.2	Rough	55
5	4 / 16	250 / 25	180	1.2	Rough	54
6	4 /16	240 / 12	180	1.2	Good	71

Table 3: Test conditions for Inpulse® 2 trials for 3.2 mm thick panels, 0.3 mm
holes, I average (I_{av}) = 4 A/dm²

Test	I forward / I reverse [A/dm²]	Pulse Parameters [ms] Forward / Reverse	Phase Shift [%]	Pulse Rise Time Factor	Frequency [Hz]	Throwing Power min. [%]
1	5.3 / 16	DC	-	-	-	30
2	5.3 / 16	40 / 2	180	1.2	23.8	40
3	5.3 / 16	80 / 4	180	1.2	11.9	50
4	5.3 / 16	160 / 8	180	1.2	6.0	60
5	5.3 / 16	240 / 12	180	1.2	4.0	70

Table 4: Pulse plating bath sequence for thick panel trials

Sequence	Exposure time [min]	A/dm² Ratio Forward to Reverse	Pulse timing [ms]
1	100	1 : 3	30 : 1.5
2	15	1 : 2.5	20 : 1
3	5	1 : 1.1	20 : 1

Claims:

1. Method of electroplating a workpiece comprising high-aspect ratio holes, the method comprising:

5

   a. bringing the workpiece and at least one anode into contact with a metal plating electrolyte, and

   b. applying a voltage between the workpiece and the anodes, to the effect that a current flow is provided to the workpiece, wherein the

10   current flow is a pulse reverse current flow having a frequency of at most about 6 Hertz with, in each cycle time, at least one forward current pulse and at least one reverse current pulse.

2. Method according to claim 1, comprising setting the ratio of the duration of

15   the forward current pulses to the duration of the reverse current pulses of one cycle in a range from about 5 to about 75.

3. Method according to any one of the preceding claims, comprising setting the duration of the forward current pulses of one cycle to at least about 100 ms.

20

4. Method according to any one of the preceding claims, comprising setting the duration of the reverse current pulses of one cycle to at least about 0.5 ms.

5. Method according to any one of the preceding claims, comprising setting the

25   peak current density of the forward current pulses at the workpiece in a range from about 3 A/dm² to about 15 A/dm².

6. Method according to any one of the preceding claims, comprising setting the peak current density of the reverse current pulses at the workpiece in a

30   range from about 10 A/dm² to about 60 A/dm².

7. Method according to any one of the preceding claims, comprising

a. applying a first voltage to between a first side of the workpiece and at least one first anode, to the effect that a first pulse reverse current flow is provided to the first side of the workpiece, said first pulse reverse current flow having at least one first forward current pulse and at least one first reverse current pulse flowing in each cycle time, and

b. applying a second voltage to between a second side of the workpiece and at least one second anode, to the effect that a second pulse reverse current flow is provided to the second side of the workpiece, said second pulse reverse current flow having at least one second forward current pulse and at least one second reverse current pulse flowing in each cycle time.

8. Method according to claim 7, comprising offsetting the first forward and reverse current pulses relative to the second forward and reverse current pulses, respectively.

9. Method according to claim 8, comprising offsetting the first current pulses relative to the second current pulses by approximately 180°.

10. Method according to any one of the preceding claims, comprising providing the current flow, in each cycle time, with two forward current pulses and one reverse current pulse with one zero current break between the two forward current pulses.

11. Method according to any one of the preceding claims, comprising varying, in the course of metal plating the workpiece, at least one parameter of the pulse reverse current flow, selected from the group comprising the ratio of the duration of the forward current pulses to the duration of the reverse current pulses of one cycle and the ratio of the peak current density of the forward current pulses to the peak current density of the reverse current pulses.

12. Method according to claim 11, comprising increasing, in the course of metal plating the workpiece, the ratio of the peak current density of the forward current pulses to the peak current density of the reverse current pulses, and/or decreasing, in the course of metal plating the workpiece, the ratio of the duration of the forward current pulses to the duration of the reverse current pulses of one cycle.

13. Method according to any one of the preceding claims, comprising bringing the workpiece into contact with the metal plating electrolyte by delivering the metal plating electrolyte towards the surface of the workpiece at an electrolyte flow velocity relative to the surface of the workpiece.

14. Method according to claim 13, comprising forcing the metal plating - electrolyte under agitation towards the workpiece.

15. Method according to any one of claims 13 and 14, wherein the electrolyte flow velocity at the surface of the workpiece comprises a velocity component normal to the surface of the workpiece being at least about 1 m/sec.

16. Method according to any one of the preceding claims, wherein the anodes are inert and dimensionally stable.

17. Method according to any one of the preceding claims, wherein the metal plating electrolyte is a copper plating electrolyte.

18. Method according to claim 17, wherein the copper plating electrolyte contains at least one compound capable of oxidizing copper metal to copper ions and wherein additional copper metal pieces are brought into contact with the copper plating electrolyte.

19. Method according to claim 18, wherein the compounds capable of oxidizing copper metal to copper ions are ferric compounds.
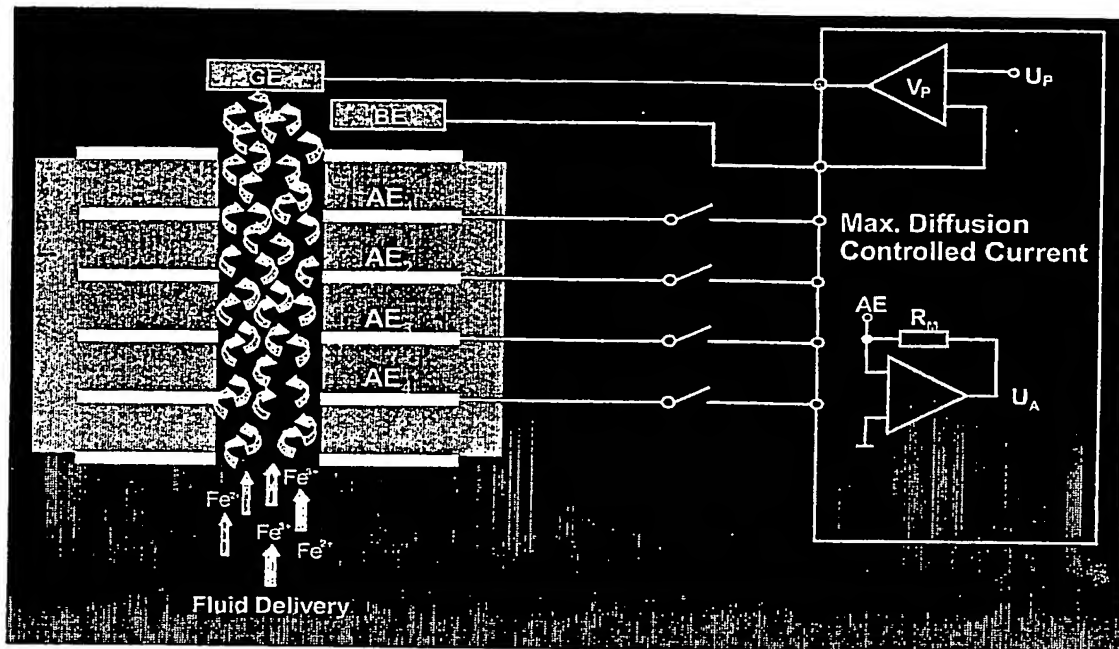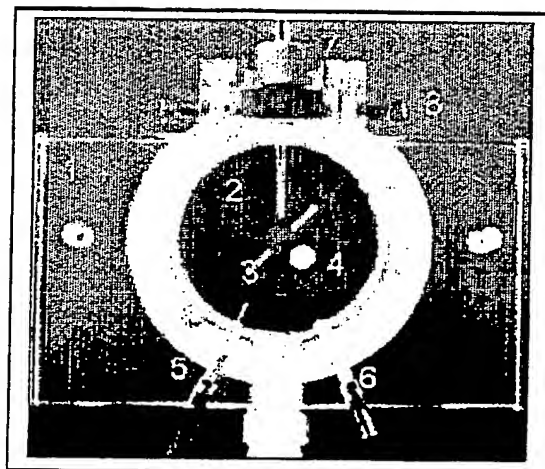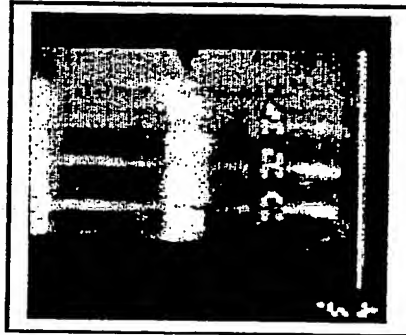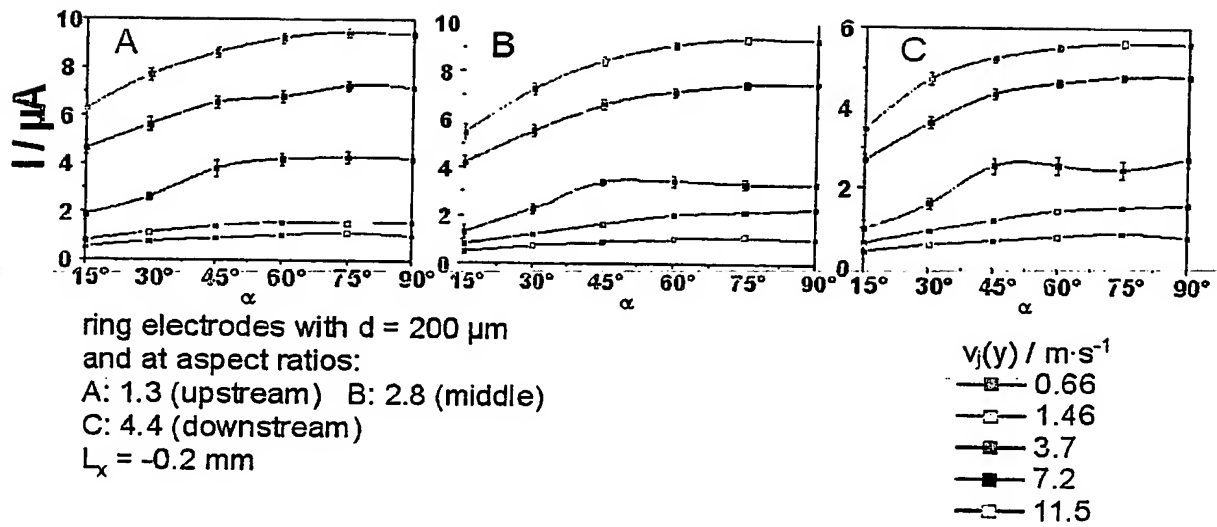
Fig. 1

Fig. 2

Fig. 3
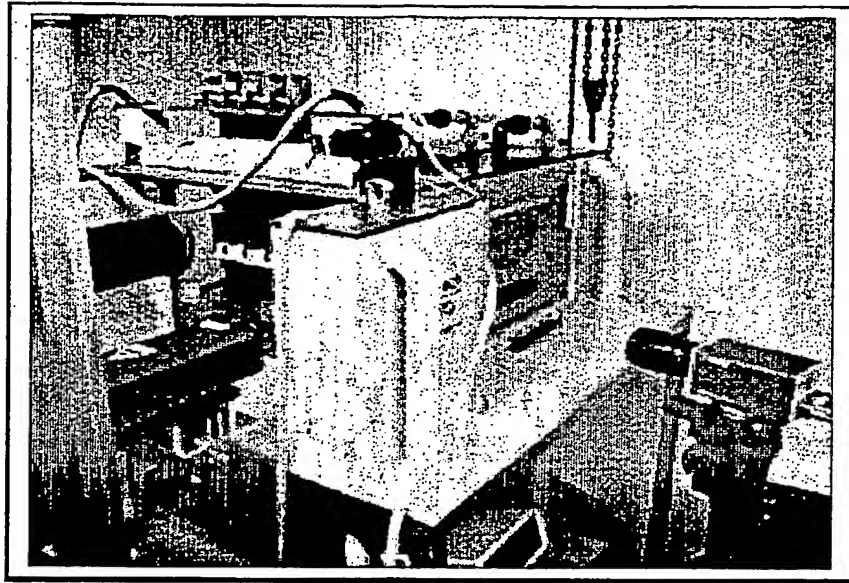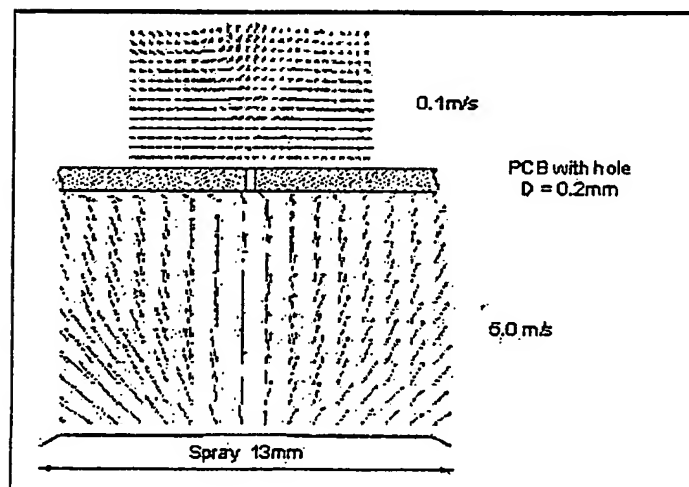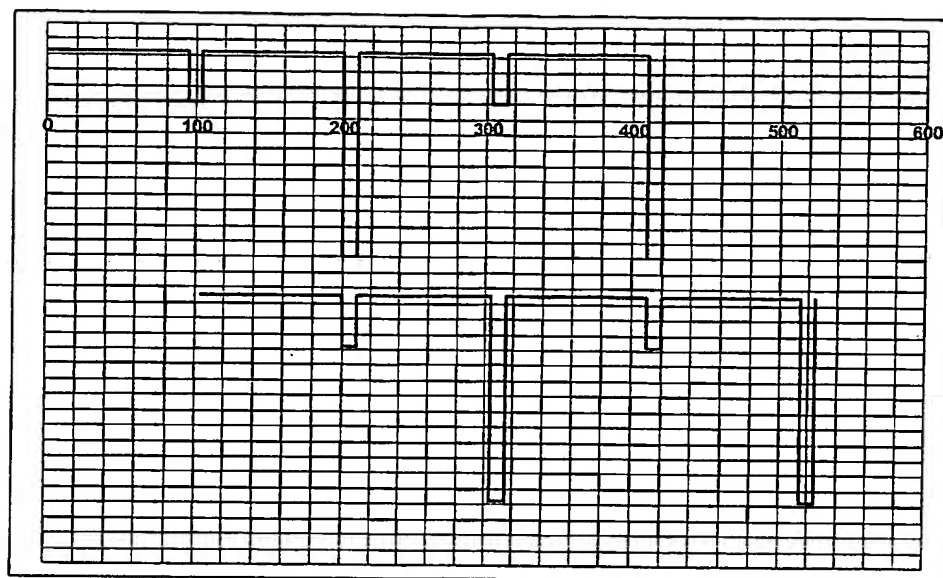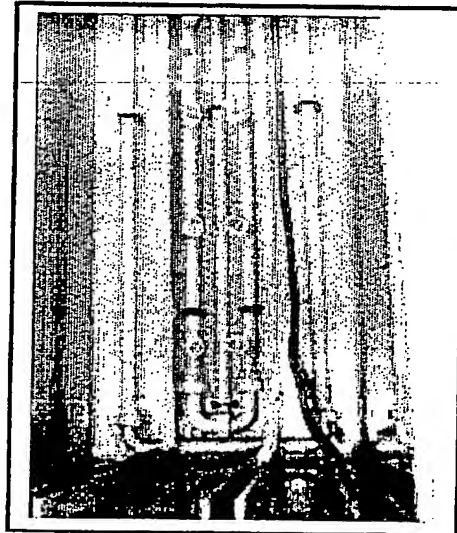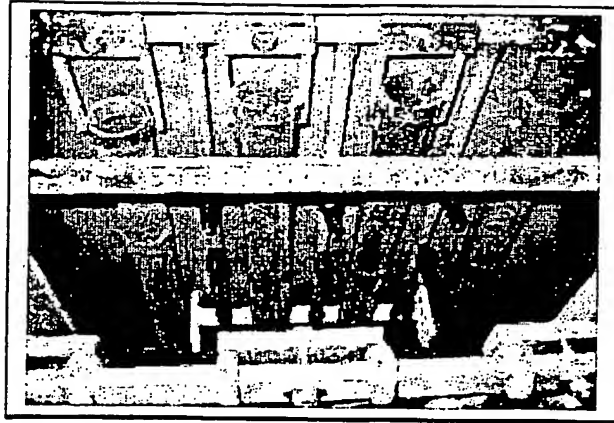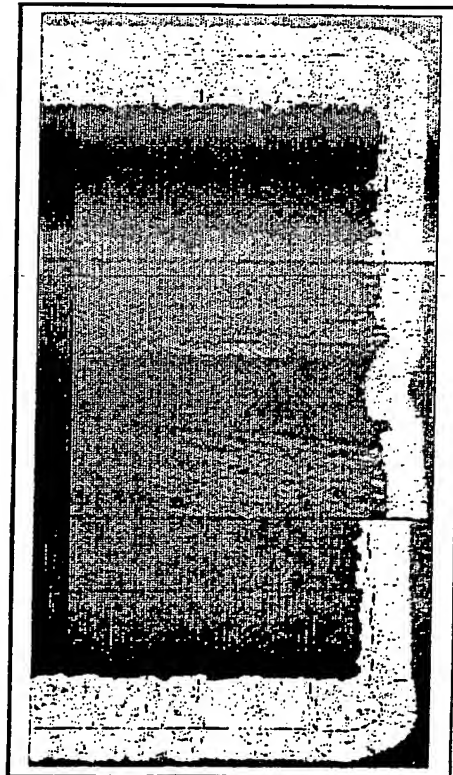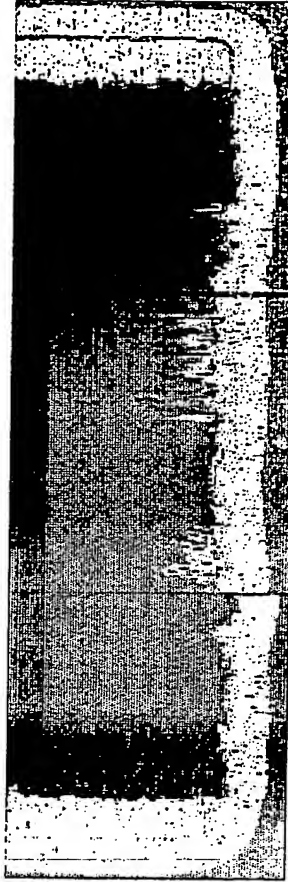
ring electrodes with d = 200 µm
and at aspect ratios:
A: 1.3 (upstream)   B: 2.8 (middle)
C: 4.4 (downstream)
$L_x = -0.2$ mm

$v_j(y) / m \cdot s^{-1}$
—■— 0.66
—□— 1.46
—■— 3.7
—■— 7.2
—□— 11.5

Fig. 4

Fig. 5

0.1m/s

PCB with hole
D = 0.2mm

5.0 m/s

Spray 13mm

Fig. 6

Fig. 7

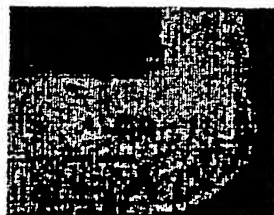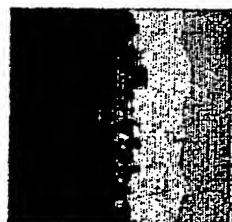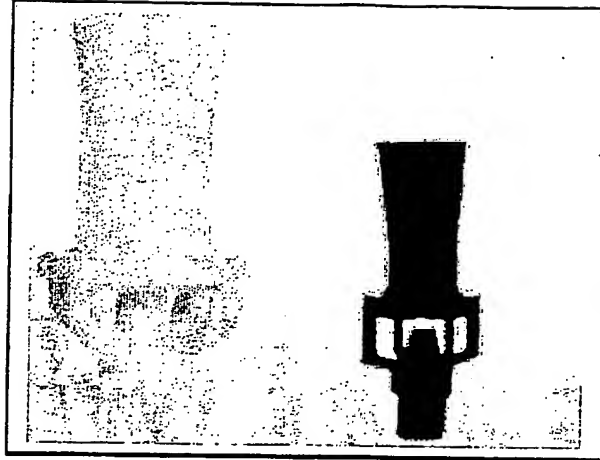Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25D7/12 C25D5/18 H05K3/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L C25D H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.	[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
14 July 2004	22/07/2004

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Zech, N

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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